

ANOMALOUS RESISTIVITY AT THE STRUCTURAL
PHASE TRANSITION OF POLYCRYSTALLINE SnTe

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ABSTRACT

An excess resistivity has been observed in thin film polycrystalline samples of SnTe with low carrier concentration and is attributed to the additional scattering due to the phonon softening associated with the structural phase transition.

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The structural phase transition from the rock-salt to the rhombohedral structure in SnTe is distinguished by its marked dependence on carrier concentration in the samples studied. Early indications of the phase transition (Novikova and Shelimova 1966) in an anomalous expansion coefficient were only proved valid much later by a neutron scattering study (Iizumi et al 1975) of the temperature dependence of the rhombohedral distortion in the material in a low carrier concentration form. The distortion was found to decrease as the temperature increased from 0 K, dropping smoothly to zero in a second order phase transition at 98 K. Subsequent studies of the transition by anomalies in the resistivity (Kobayashi et al 1975), in the average band gap as deduced from the optical dielectric function far from the fundamental absorption edge (Murase et al 1978), and in Raman scattering (Murase et al 1978) have been fitted (Kawamura 1979) with an expression extrapolating to values of 125 K for the structural phase transition temperature at zero carrier concentration. Such measurements have all, however, been carried out on single crystals of the compound.

We have examined the temperature dependence of the resistivity of polycrystalline films of typical thickness 3500 Å produced by thermal evaporation of the compound onto glass substrates held at temperatures up to 200 °C. It has been shown (Todoroki and Onuma 1974) that increased substrate temperature during deposition leads to a decrease in the carrier concentration of the material, presumably by decreasing the Sn vacancy concentration held to be the origin of the degenerate p-type carriers.

The results for typical samples in the high and low carrier concentration regimes are shown in figure 1. It can be seen that the film with a carrier concentration $p^* \frac{1}{R_H e}$, where R_H is the Hall constant measured in a field of 5.5 kG at 77 K) of $1.15 \cdot 10^{21} \text{ cm}^{-3}$ shows the monotonic decrease with temperature to be expected from a degenerate hole gas with acoustic phonon scattering being dominated by charge impurity scattering as $T \rightarrow 0$. Kobayashi

et al. (1975) found that a decrease of the carrier concentration to $1.2 \times 10^{20} \text{ cm}^{-3}$ led to the emergence of an extra component in the resistivity centred about 98 K which was explained (Katayama 1976 and Kobayashi et al 1975) in terms of the scattering of the holes at the Fermi energy by the transverse optic phonons associated with the structural phase transition as they softened to low frequencies in the neighbourhood of $\underline{k} = (\frac{2\pi}{a}, 0, 0)$ (where a is the lattice constant of SnTe) as the temperature decreased, increasing again in the rhombohedral phase.

The resistivity anomaly in figure 1 for the sample with the lower carrier concentration ($p^* = 7.60 \times 10^{19} \text{ cm}^{-3}$) is centred around a temperature of 145 K and is appreciably larger than that reported by Kobayashi et al. To the accuracy of measurement, ($\pm 4\%$), the Hall constant of this sample was found to be independent of temperature in the temperature range up to 220 K, indicating that the anomaly observed cannot be explained by an unusual variation in the carrier concentration with temperature. Further justification for identifying this added resistivity with the structural phase transition comes from the fact that $\left| \frac{d\rho}{dT} \right|_{T < 140 \text{ K}} = \frac{1}{2} \left| \frac{d\rho}{dT} \right|_{T > 140 \text{ K}}$, as is to be expected at such a structural phase transition from the dependence of the square of the TO phonon frequency on temperature.

$$\begin{aligned} \omega_{\text{TO}}^2 &= \alpha (T - T_c) & (T > T_c) \\ \omega_{\text{TO}}^2 &= 2 \alpha (T_c - T) & (T < T_c) \end{aligned}$$

The larger magnitude of the anomaly in absolute terms ($\Delta \rho \sim 1.2 \times 10^{-4} \Omega \text{ cm}$) in comparison with the result of Kobayashi et al ($\Delta \rho \sim 1.8 \times 10^{-6} \Omega \text{ cm}$) despite a carrier concentration ratio of only 1.5 can be partially explained in terms of the sample with the lowest k_F experiencing a greater frequency decrease as the phonons with comparable wave numbers soften than would be the case for larger k_F . This has been discussed in quantitative terms by Katayama (1976) who calculated the added resistivity as a function of

$$\gamma = \frac{4A k_F^2}{\alpha} \quad \text{where } \alpha \text{ is given above and } A \text{ describes the dispersion in } \frac{\omega}{T}$$

space of the TO phonon. If, in our case, we take the value of A to be the same as that of Kobayashi et al., we would expect to find an anomaly a factor of approximately 2.6 greater than that of Kobayashi et al., due to the difference in carrier concentrations in the samples, appreciably smaller than that observed. However, Katayama deduces a value for A from the data of Kobayashi et al which is an order of magnitude less than that measured in neutron spectroscopy (Pawley et al. 1966). We would argue that this indicates an appreciable anisotropy of the phonon softening, in agreement with calculations of the anomalous specific heat at the phase transition (Loram and Yaraneri 1979) which show anomalies orders of magnitude larger than observed (Hatta and Rehwald 1977 and Hatta and Kobayashi 1977) if an isotropic softening of the phonon spectrum is assumed. Since our samples are polycrystalline, it might be expected that the anisotropy of softening is reduced in our samples, leading to a larger fraction of the phase space of the phonons showing softening, and hence leading to a larger resistivity anomaly.

Further investigations in the intermediate range of carrier concentrations are in hand.

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Figure Captions

Figure 1 - Temperature dependence of resistivity of typical samples, the carrier concentrations being as shown. The two lines running through the data for the lower carrier concentration sample have gradients in the ratio 2:1 above and below 145 K.

